Electrolytic Synthesis of Iodoform

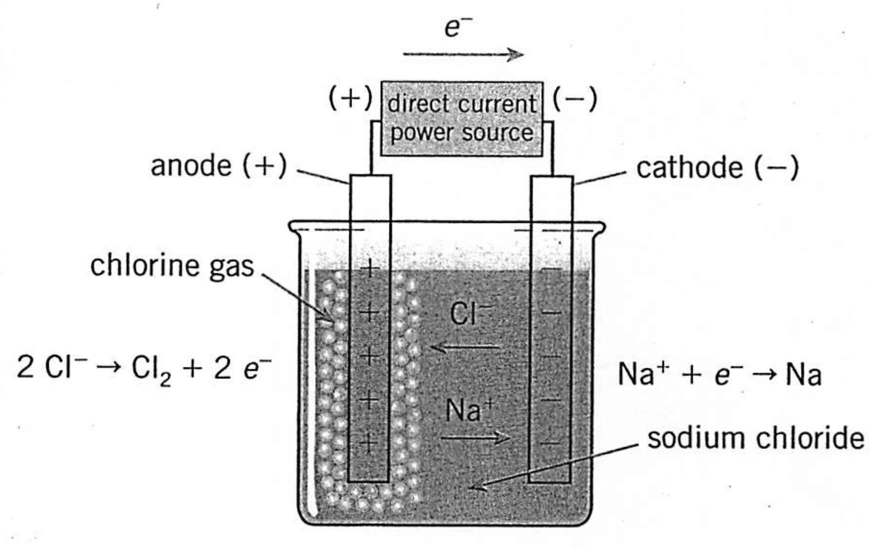
PURPOSE

- Perform an electrolysis of potassium iodide with acetone in basic solution to form iodoform
- Analyze and explain the products of oxidation and reduction in the experimental electrolysis

INTRODUCTION

In an **electrolytic cell**, electrical energy is used to cause a chemical change. In a sense, this process is the opposite of that in a **galvanic cell**, where chemical differences cause an electrical current to flow. In electrolytic cells, positively charged cations move toward the negatively charged **cathode**, where extra electrons are pumped to create a surplus. Typically, the positively charged cations are reduced to the metallic atom. Negatively charged anions move toward the positively charged **anode**, where there is a shortage of electrons. The anions are frequently oxidized to their nonmetal atom. These migrations of ions are illustrated in Figure 16.1, a schematic rendering of an electrolytic cell consisting of molten sodium chloride.

Figure 16.1
Electrolytic Cell



One of the most important applications of electrolytic cells to the industrial world is the electrolysis of brine, a concentrated solution of sodium chloride, the source of which is seawater. The process thus converts an inexpensive and common raw material into commercially valuable products such as the gases hydrogen and chlorine, as well as sodium hydroxide solution. Chlorine is in turn used in the manufacture of plastics and to chlorinate water for safe drinking. Sodium hydroxide, the most important industrial base, is used in many processes, including the neutralization of acids and the manufacture of paper and soap.

Note that there is the potential for competition for electrons at the electrodes of an aqueous electrolytic cell. At the cathode, the cation of the salt can be reduced. Alternatively, if there is an energy advantage, the water can be reduced to hydrogen gas with formation of base (hydroxides) as a by-product. At the anode, too, there may be competition. Either the anion of the salt can be oxidized, or the water can be oxidized to oxygen gas with formation of acid as a by-product. For the electrolysis of brine, then, the possibilities are as follows.

At cathode:

$$Na^+_{(aq)} + e^- \rightarrow Na_{(s)} \qquad E° = -2.71\ V$$

or

$$2\ H_2O_{(l)} + 2\ e^- \rightarrow H_{2(g)} + 2\ OH^-_{(aq)} \qquad E° = -0.83\ V$$

At anode:

$$2\ Cl^-_{(aq)} \rightarrow Cl_{2(s)} + 2\ e^- \qquad E° = -1.36\ V$$

or

$$2\ H_2O_{(l)} \rightarrow O_{2(g)} + 4\ H^+_{(aq)} + 4\ e^- \qquad E° = -1.23\ V$$

Note that the chloride and the water are oxidized with similar facility, assuming that the chloride concentration is 1 *M*. To ensure that the chloride is oxidized in the commercial process, rather than the water, the concentration of sodium chloride is kept very high.

The overall desired electrolytic reaction, then, is

$$2\ H_2O_{(l)} + 2\ e^- \rightarrow H_{2(g)} + 2\ OH^-_{(aq)} \qquad E° = -0.83\ V$$

$$2\ Cl^-_{(aq)} \rightarrow Cl_{2(s)} + 2\ e^- \qquad E° = -1.36\ V$$

yielding

$$2\ Cl^-_{(aq)} + 2\ H_2O_{(l)} \rightarrow H_{2(g)} + Cl_{2(s)} + 2\ OH^- \qquad E° = -2.19\ V$$

Procedure Preview For the preparation of iodoform in this experiment, an electrolysis of aqueous potassium iodide solution is first performed. Freshly prepared iodine, a product of the electrolysis, then reacts with acetone in basic solution to form iodoform, acetate anion, and iodide anion:

$$CH_3COCH_{3(l)} + 3\ I_{2(s)} + 4\ OH^-_{(aq)} \rightarrow CHI_{3(s)} + CH_3COO^-_{(aq)} + 3\ I^-_{(aq)} + 3\ H_2O_{(l)}$$

Pre-Lab Questions

1. What is a **ketone**? How are ketones named?

2. Determine the formula and draw a molecular sketch of:

   a. acetone

   b. acetate ion

   c. iodoform

   d. triiodomethane

   e. chloroform

   f. tribromomethane

3. For the electrolysis of an aqueous solution of KI, write a balanced equation to show the reaction at

   a. the anode ______________________________

   b. the cathode ______________________________

MATERIALS

- battery
- potassium iodide (KI)
- two pencil leads
- 50-mL beaker
- filter paper
- acetone (CH_3COCH_3)
- 0.1 *M* potassium hydroxide (KOH)
- two wires (each with an alligator clip at each end)
- #8 rubber stopper
- microstir bar *(see Appendix C on page 140)*

PROCEDURE

Step A Obtain a 50-mL beaker and position it on a magnetic stir plate. Add 1.000 g KI and 10 mL distilled water to beaker and mix thoroughly with microstir bar. Add 1.5 mL acetone and mix. Add 0.5 mL KOH and mix.

Step B Place a #8 rubber stopper on the beaker. Obtain two pencil leads, positioning one down each side of the stopper such that the end of the lead is immersed in the solution below. Each pencil lead, an electrode, should touch the solution, but not touch either the other electrode or the microstirbar. Use the alligator clip at one end of each wire to fix the lead electrodes in the desired position.

Step C Attach the opposite end of each wire by its alligator clip to a battery terminal.

Step D Allow electrolysis for at least 10 minutes. Record time elapsed in seconds.

Step E Collect the solid product onto filter paper by gravity filtration. Dry in air overnight.

Step F Find the mass of the product.

Step G Perform a melting point analysis of the solid product.

Calculations

1. Calculate the number of moles of iodoform produced.
2. Calculate the number of moles of electrons required to produce the iodoform.
3. Calculate the number of coulombs required to produce the iodoform.
4. Calculate the number of amperes required of the battery to produce the iodoform.

Post-Lab Questions

1. What is the product of oxidation during the electrolysis? Write and balance an equation to show this. Did you collect this product?
2. What is the product of reduction during the electrolysis? Write and balance an equation to show this. Did you collect this product?
3. Why did you add a small amount of KOH before starting the procedure?
4. How can you be sure that the electrodes were nonreactive—that is, that they did not participate in the reaction?
5. Determine the limiting factor in this experiment. Explain or show calculations to support your contention. Is it possible to calculate the percent yield?
6. Would you expect to attain 100% yield in this experiment? Why or why not?
7. Is iodoform a polar molecule? Draw a **Lewis structure** (apply VSEPRT) to support your contention.
8. Compare the experimental melting point to the theoretical value (found in the *CRC* or other handbook). Calculate percent error.